PHASE EQUILIBRIA OF 1,1,1-TRIFLUOROETHANE (HFC-143a) + PROPANE (HC-290)

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Abstract

Isothermal vapor-liquid equilibrium data for the binary mixture of 1,1,1-trifluoroethane (HFC-143a) + Propane (HC-290) were measured at six equally spaces temperatures of 268.15, 278.15, 288.15, 298.15, 308.15 and 318.15K by using a circulation-type equilibrium apparatus. The phase composition at equilibrium was measured by gas chromatograph. The experimental data were compared with the calculated data based on the Carnahan-Starling-De Santis (CSD) equation of state. Good agreement between experimental and calculated data indicates that CSD EOS can be used well to estimate the thermodynamic properties for the mixture of HFC-143a + propane. This binary system of HFC-143a + propane exhibits azeotropes through the temperature range studied here.

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Introduction

For nearly sixty years, chlorofluorocarbons, or CFCs, have been widely used as solvents, foam blowing agents, aerosols and specially refrigerants due to their preeminent properties such as stability, non-toxicity, non-flammability, good thermodynamic properties and so on. However, they also have harmful effect on the Earth's protective ozone layer. So, they have been being regulated internationally by Montreal Protocol since 1989. Subsequently, it was discovered that CFCs also contributed significantly to the global warming problem. The result was that CFCs have been forbidden in developed from January of 1996. In 2010, producing and using of CFCs will be prohibited completely in all over the world. In consequence, lots of research have been done to find the suitable replacement for CFCs. Initial alternatives included some hydrochlorofluorocarbons (HCFCs), but they will be also phased out internationally around 2020 ~ 2030 because their ozone depletion potentials and global warming potentials are in relative high levels though less than those of CFCs. Hydrofluorocarbons (HFCs) - synthetic refrigerants which have zero ozone depletion potentials - were proposed as promising replacements for CFCs and HCFCs. Hydrofluorocarbons such as difluoroethane (HFC-32), pentafluoroethane (HFC-125), 1,1,1,2-tetrafluoroethane (HFC-134a), 1,1,1-trifluoroethane (HFC-143a), 1,1-difluoro-ethane (HFC-152a), and 1,1,1,2,3,3,3-heptafluoropropane (HFC-227ea) are promising alternative refrigerants in place of dichlorodifluoromethane (CFC-12) and chloro-difluoromethane (HCFC-22). Their global warming potentials (GWP) are less than those of CFC-12 and HCFC-22 because they contain more hydrogen atoms and thus have a shorter atmospheric lifetime. Unfortunately, HFCs are stable but very expensive and the manufacture of these HFCs is high-tech process and consequently their cost is high, which would cause a burden for the poor countries. On the other hand, the utilization of hydrocarbons such as propane, n-butane, iso-butane, propylene, etc. as effective refrigerants is believed as an alternative solution because these hydrocarbons are environmentally benign chemicals (due to their zero ozone depletion potentials and near zero global warming potentials) and have many outstanding properties. Moreover, they are common components of natural gas, so they are cheap and plentiful. Their flammability has caused some concerns but all tests done so far indicated that they are so quite safe in small applications such as domestic fridge and car air-conditioner due to the very small amounts involved [1]. Therefore, the mixture of the two compounds may have a good potential for alternative refrigerants. Vapor-liquid equilibrium data are required as one of the most important types of basic information in evaluating the performance of refrigeration cycles and determining their optimal compositions.

In this work, VLE data for HFC-143a + propane had been measured, and the experimental data were correlated with the Carnahan-Starling-De Santis (CSD) equation of state (EOS). Almost all the calculated values using this model give good agreement with the experimental data. This mixture exhibits azeotropes. In the range of experimental temperature, the average absolute deviations of pressures and vapor phase compositions between experimental and calculated values were determined and the relevant parameters were presented.

Experimental Section

The vapor-liquid equilibrium apparatus used in this work was a circulation-type one in which both liquid and vapor phase were recirculated continuously. Experimental apparatus and procedure were explained well in our previous work [2-5].

Correlation

In this work, the experimental VLE data were correlated with the CSD EOS that has been demonstrated to represent the P-V-T properties of the eleven halogenated hydrocarbon refrigerants and their mixtures investigated very well [6].
This EOS is expressed as follows:

$$\frac{\mathrm{PV_M}}{\mathrm{RT}} = \frac{1+y+y^2-y^3}{(1-y)^3} - \frac{\mathrm{a}}{\mathrm{RT}(\mathrm{V_M}+\mathrm{b})} \tag{1}$$

$$\mathrm{y} = \mathrm{b}/4\mathrm{V_M}, \quad \mathrm{V_M}\text{: molar volume} \tag{2}$$

In case of pure component, the temperature dependence of ‘a’ and ‘b’ are represented by the following forms:

$$\mathrm{a} = \mathrm{a_0}\exp\left(\mathrm{a_1T} + \mathrm{a_2T^2}\right) \tag{3}$$

$$\mathrm{b} = \mathrm{b_0} + \mathrm{b_1T} + \mathrm{b_2T^2} \tag{4}$$

The CSD EOS using the approach of Morrison and McLinden[6] was adopted in correlating VLE data. The coefficients of a_o, a_1, a_2, in equation (3) and b_o, b_1, b_2 in equation (4) were cited from REFPROP 5.0 [7]. In the application of CSD EOS to mixture, there exists the effective molecular parameters a_m and b_m (the m subscript refers to the mixture) defined by using the following mixing rules:

$$a_m = \sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j a_{ij} \quad (5) \qquad b_m = \sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j b_{ij} \quad (6)$$

Where n is the number of components in mixture. When i = j, the value of a_{ii} and b_{ii} are those of 'a' and 'b' of the pure components which are determined by equation (3) and (4). The values of a_{ij} and b_{ij} can be obtained if nearly any experimental property of the mixture is known. For the binary systems, the values of a_{12} and b_{12} can be expressed as following forms:

$$a_{12} = (1 - f_{12})(a_{11}a_{22})^{1/2} \quad (7) \qquad b_{12} = \frac{1}{8}\left(b_1^{1/3} + b_2^{1/3}\right)^3 \quad (8)$$

The mixing rule for the 'a' parameter for a mixture involves the interaction parameter, f_{12}, which must be determined from experimental data. The approach is to find the value of f_{12}, which minimizes the sum of square Γ of relative deviation between measured and calculated quantities:

$$\Gamma(T,x,f_{12}) = \omega_P\left(\frac{P_{exp.} - P_{cal.}}{P_{exp.}}\right)^2 + \omega_L\left(\frac{V_{L,exp.} - V_{L.cal.}}{V_{L,exp.}}\right)^2 + \omega_v\left(\frac{V_{v,exp.} - V_{v,cal.}}{V_{v,exp.}}\right)^2 + \omega_y\left(y_{exp.} - y_{cal.}\right)^2 \quad (9)$$

Because the vapor composition must be between zero and unity, the last term in equation (9) is expressed as an absolute error. Moreover, the experimental data of vapor and liquid specific volume indicated in this equation are not available, the corresponding weighting factors in the expression of Γ are set to zero.

$$\Gamma(T,x,f_{12}) = \omega_P\left(\frac{P_{exp.} - P_{cal.}}{P_{exp.}}\right)^2 + \omega_y\left(y_{exp.} - y_{cal.}\right)^2 \quad (10)$$

Results and discussion

Some characteristic properties of pure HFC-143a and Propane from the database REFPROP 6.01 [8] which is considered to be reliable for the pure compounds considered here and consistent with other literature data are summarized in Table 1. The saturated vapor pressure of HFC-143a and Propane at various temperatures that were experimentally measured and obtained from database REFPROP 6.01 and ASHRAE [9] are shown in Table 2. The comparison between experimental and calculated values indicates that the absolute deviations of vapor pressure for both HFC-143a and Propane

Table 1. Characteristic properties [a]

Component	Chemical formula	M.W.	T_c/K	P_c/MPa	ϖ
HFC-143a	CF_3CH_3	84.04	346.04	3.776	0.2611
Propane	C_3H_8	44.10	369.85	4.248	0.1524

[a] RERPROP 6.01

Table 2. Comparison of the measured pure components vapor pressures with data from the database REFPROP 6.01 [8] and ASHRAE [9].

T (K)	Measured	REFPROP	ΔP [a] (MPa)	ΔP/P(%)	ASHRAE	ΔP [a] (MPa)	ΔP/P(%)
			HFC-143a				
268.15	0.5292	0.5284	0.0008	0.1512	-	-	-
278.15	0.7224	0.7217	0.0007	0.0969	-	-	-
288.15	0.9620	0.9637	0.0017	0.1767	-	-	-
298.15	1.2618	1.2618	0.0000	0.0000	-	-	-
308.15	1.6198	1.6244	0.0046	0.2840	-	-	-
318.15	2.0548	2.0596	0.0048	0.2336	-	-	-
Average deviation			0.0021	0.1570			
			Propane				
268.15	0.4079	0.4059	0.0020	0.4903	0.4061	0.0018	0.4413
278.15	0.5494	0.5510	0.0016	0.2912	0.5512	0.0018	0.3276
288.15	0.7350	0.7314	0.0036	0.4898	0.7316	0.0034	0.4626
298.15	0.9548	0.9519	0.0029	0.3037	0.9521	0.0027	0.2828
308.15	1.2130	1.2180	0.0050	0.4122	1.2179	0.0049	0.4039
318.15	1.5308	1.5340	0.0032	0.2090	1.5343	0.0035	0.2286
Average deviation			0.0030	0.3660		0.0030	0.3578

$^{a}\Delta P = P_{exp} - P_{cal}$, $^{b}\Delta P/P(\%) = 100\times\left[\left(P_{\exp} - P_{cal}\right)/P_{\exp}\right]$

were within ± 0.0050 MPa and the average relative deviations (ΔP/P(%)) were 0.157% for HFC-143a and 0.366% for Propane from database REFPROP 6.01[8] and 0.357% for propane from ASHRAE [9]. Interaction parameters (f_{12}) of CSD EOS with various temperatures were obtained by using experimental VLE data. The f_{12} values calculated by CSD EOS and deviations of pressure and vapor phase composition between experimental and calculated data at various temperatures are listed in Table 3.

Table 3. Values of Binary Parameters and Average Deviations of *P* and *y*

T/K	CSD EOS			
	$f_{12}{}^{a}$	δP^{a}(MPa)	$\delta P/P^{b}$(%)	δy^{c}
268.15	0.1166	0.0036	0.61	0.0056
278.15	0.1169	0.0044	0.57	0.0037
288.15	0.1181	0.0045	0.44	0.0033
298.15	0.1161	0.0044	0.33	0.0021
308.15	0.1155	0.0087	0.54	0.0037
318.15	0.1166	0.0094	0.46	0.0040

$^{a}\delta P = \frac{1}{N}\sum\left|\left(P_{exp} - P_{cal}\right)\right|$, $^{b}\delta P/P = \frac{1}{N}\sum\left|\left(P_{exp} - P_{cal}\right)/P_{exp}\right| \times 100$, $^{c}\delta y = \frac{1}{N}\sum\left|y_{\exp} - y_{cal}\right|$.

P-x-y diagram for the mixture HFC-143a + Propane at various temperatures of 268.15, 278.5, 288.15, 298.15, 308.15 and 318.15K are shown in Figure 1. The black dash lines represent the calculated data by CSD EOS. And the black dash-point-dash line represent the S. Bobbo’s work [10] at 283.15 K. As can be seen in this figure, the calculated diagram did not coincide exactly with the corresponding experimental data.

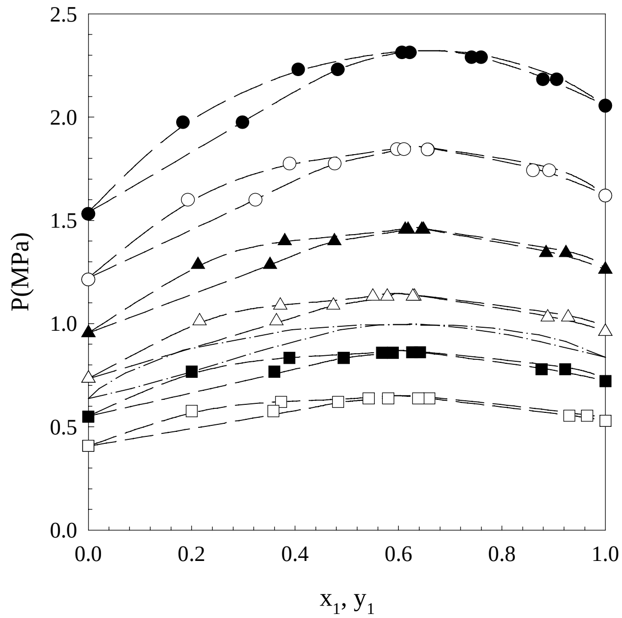
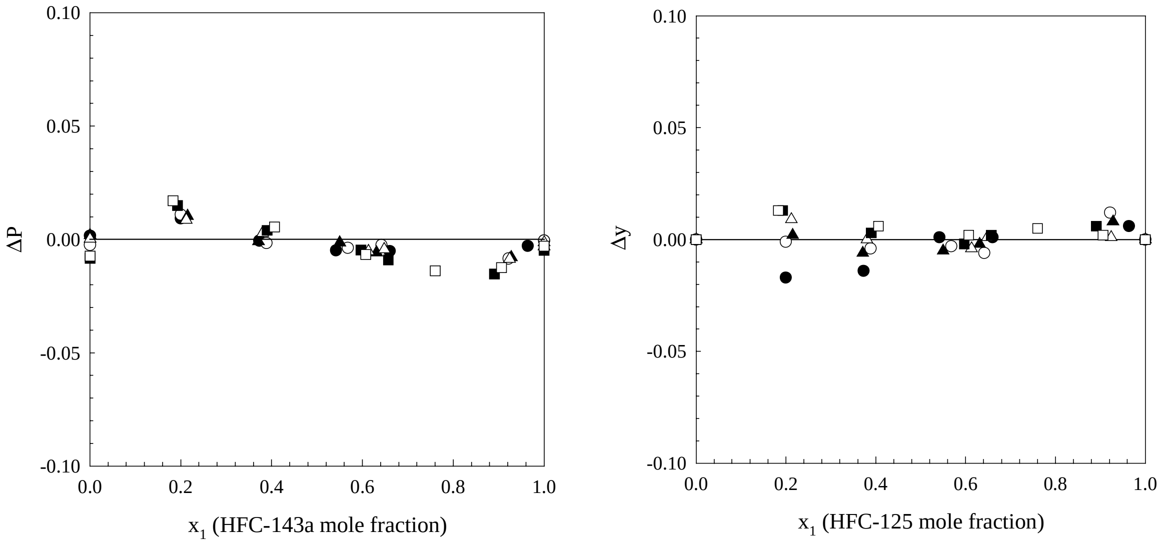


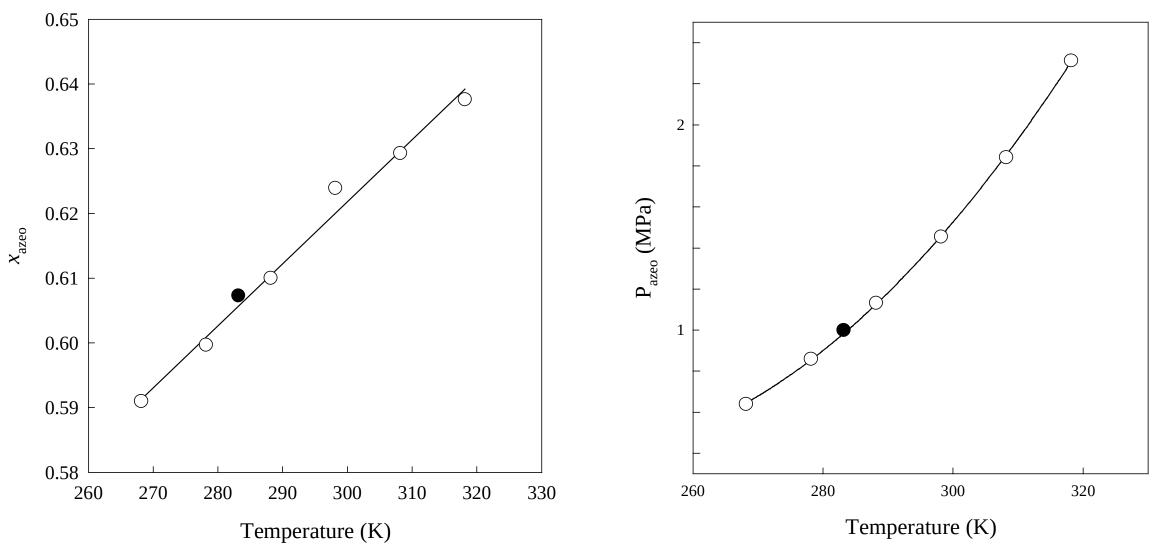
Figure 1. P-x-y diagram for the mixture of HFC-143a + Propane at various temperatures; (●) 268.15 K, (○) 278.15 K, (▲) 288.15 K, (△) 298.15 K, (■) 308.15 K, (□) 318.15 K, (---) calculated value by using CSD EOS, (|.|) S. Bobbo's work at 283.15 K [10].

This difference can be demonstrated clearly by the deviations of vapor phase composition and pressure of the experimental data from the correlated value using CSD EOS in each point, which are shown in Figure 2. The interaction parameters and the average deviations of pressure and vapor phase composition between measured and calculated values for the mixture of HFC-143a and Propane are reported in Table 3. It indicates that in the temperature range from 268.15 to 318.15K, the average deviation of pressure and vapor phase composition between measured and calculated values by CSD EOS are relatively low and acceptable. In other way, the calculated values using the CSD equations of state give relatively good agreement with the experimental data. The values of f_{12} determined at 268.15, 278.5, 288.15, 298.15, 308.15, and 318.15K were 0.1166, 0.1069, 0.1181, 0.1161, 0.1155, and 0.1166, respectively. This mixture exhibited the azeotropes. Azeotropic data of this mixture have been determined at the composition range from 0.591 to 0.637 mole fraction, and at the pressure range from 0.639 to 2.314 MPa in the temperature from 268.15 to 318.15 K. Azeotropic compositions and pressures depended on the temperature. In the range of experimental temperature, azeotropic compositions were correlated by the empirical equation, x_{azeo}=0.334+ 9.591×10^{-4}T, and azeotropic pressures were correlated by the empirical equation, P_{azeo}= 17.8820.146T+$3.067\times10^{-4}T^2$. Azeotropic compositions and pressures were shown in Table 4 and Figure 3. After all, we can confirm that the CSD EOS demonstrates well the thermodynamic properties of the mixture of HFC-143a + Propane in the temperature range between 268.15 and 318.15 K.



(a) (b)

Figure 2. Deviation of the mixture of HFC-143a + Propane at various temperatures; (a) deviation of pressure, (b) deviation of vapor phase composition (●) 268.15 K, (○) 278.15 K, (▲) 288.15 K, (△) 298.15 K, (■) 308.15 K, and (□) 318.15 K.



(a) (b)

Figure 3. Variation of the azeotropic composition and pressure for HFC-143a + Propane mixture; (○) this work, (●) S. Bobbo's work at 283.15 K [10].

Table 4. Azeotropic Data of the HFC-143a + Propane System

	T(K)	x_{azeo}	P_{azeo}(MPa)
This work	268.15	0.5910	0.6397
	278.15	0.5997	0.8594
	288.15	0.6100	1.1320
	298.15	0.6239	1.4551
	308.15	0.6293	1.8426
	318.15	0.6376	2.3139
S. Bobbo's work [10]	283.18	0.6073	1.0003

Conclusions

Measurements of the vapor-liquid equilibria for the mixture of HFC-143a + Propane at six equally spaces between 268.15 and 318.15K were carried out by using a circulation-type equilibrium apparatus. It was found that this mixture show azeotropic behavior in the range of temperature above. The experimental VLE data were correlated with CSD EOS and interaction parameters f_{12} were obtained. The calculated data from the CSD EOS show relatively good agreement with the experimental data. This result indicates that the CSD EOS can be used well to estimate the thermodynamic properties for the mixture of HFC-143a + Propane in the range of temperatures between 268.15 and 318.15K.

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